Pressurized Fluid Extraction for Quantitative Recovery of Chloroacetanilide and Nitrogen Heterocyclic Herbicides in Soil

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Pressurized fluid extraction (PFE) is a new sample extraction method operated at elevated temperatures and pressures with liquid solvents. The use of PFE was investigated for the extraction of four Hawaiian clayey soils fortified with the selected chloroacetanilide and nitrogen heterocyclic herbicides Alachlor, Bromacil, Hexazinone, Metribuzin, and Tebuthiuron. The effects of operation temperature, pressure, flush volume, and static cycles on PFE performance were studied. Water was the most effective modifier of PFE for quantitative recoveries of the five herbicides in soils. The simple extraction method required pretreatment of the soil with 37.6% water and subsequent two-static-cycle extraction with a total of 32 mL of acetone at 1500 psi and 100 °C. Average recoveries of Alachlor, Bromacil, Hexazinone, Metribuzin, and Tebuthiuron ranged from 93 to 103% by the water-assisted PFE, compared with only 68–83% recoveries of the corresponding chemicals when no water was used. The extraction time and total organic solvent consumption were reduced from 18 h and 300 mL by Soxhlet to 22 min or less and 80 mL or less of organic solvent by PFE.

INTRODUCTION

Environmental analysis of pesticides is important because of the wide application and possible safety hazards of these chemicals. Chloroacetanilide and nitrogen heterocyclic herbicides are widely used as weed control agents for agricultural and nonagricultural purposes (Creager, 1990; Petersen and Ueckert, 1992; Barcelò, 1993; Boyd-Boland and Pawliszyn, 1995; Randall and Sanders, 1997). The presence of these herbicides has been extensively reported in river water (Pereira et al., 1990; Kobayashi et al., 1993; Tronczynski et al., 1993), groundwater (USEPA, 1987; Pereira et al., 1990; Caldwell et al., 1993), and soils (Durand and Barcelò, 1991; Steinheimer, 1993). Groundwater is the source of drinking water for approximately 90% of rural households and 75% of cities in the United States (Barcelò, 1993). That means, in total, more than a half of US citizens rely on groundwater for their everyday needs. The chloroacetanilide and nitrogen heterocyclic herbicides are concerned over their contamination of groundwater and a high potential risk for humans and wildlife. For example, Metribuzin has been identified as an endocrine disrupter (Yamano and Morita, 1995), and its carcinogenic potential has been evaluated by the United States Environmental Protection Agency (USEPA). Bromacil has been shown to be hematotoxic and to cause aplastic anemia and thrombopemia (Parent and Thouvenot, 1993). Previous methods for the extraction and determination of the chloroacetanilide and nitrogen heterocyclic herbicides include conventional solvent and solid-phase extractions, and gas chromatographic (GC) and high-performance liquid chromatographic (HPLC) determination (Steinheimer, 1993; He and Hian, 1997; Gennaro et al., 1999).

Sample extraction procedures are often perceived as bottlenecks in analytical methods. Previously, the ex-

traction of environmental materials such as soils, sludge, and other solid wastes required large amounts of solvents. Soxhlet, for example, requires 250–500 mL of extracting solvent for most environmental samples. The organic solvents required to extract solid samples can compose the largest source of waste in environmental analysis laboratories. Recent changes in environmental regulation place severe restriction on the amount of solvent usage in analytical laboratories. In the past few years, chemists have developed alternative methods to replace the classical solvent extraction, such as automated Soxhlet extraction (Lopez-Avila et al., 1993), sonication extraction (Eiceman et al., 1980), microwave dissolution (Kingston and Jassie, 1986), and supercritical fluid extraction (SFE) (Oostdyk et al., 1993; Lopez-Avila, 1999). Each technique reduces the volume of extraction solvent required and shortens the sample preparation time as compared to conventional Soxhlet extraction.

Automated Soxhlet extraction can be faster (2–4 h) and use less solvent (50–100 mL) than conventional Soxhlet extraction. However, after extraction, analysts must manually separate extracts from the sample by filtering, centrifuging, or passing the sample through cleanup cartridges because the sample is immersed in the boiling solvent. SFE has recently received increasing interest for extracting a variety of compounds in soils and sediments with improved recovery. SFE can also reduce the amounts of hazardous solvents used because carbon dioxide is used as the principal extraction fluid. However, because of carbon dioxide's nonpolar nature, organic and inorganic modifiers are required for the extraction of intermediate to polar environmental compounds.

A pressurized fluid extraction (PFE) technique was recently developed to meet the new challenges for reducing solvent usage and decreasing analysis time. With this technique, a solid sample is manually packed

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Table 1. Basic Characteristics of the Four Silty Clay Soils Used[a]

soil series	taxonomy	pH[b]	sand[c] (>45 μm)	silt[c] (2-45 μm)	clay[c] (<2 μm)	organic carbon[c]	% moist.[d]	mineral
Honouliuli	typic chromustert	7.3	56.5	364	580	16.6	7.06	halloysite, hematite, amorphous
Nohili	cumulic haplaquoll	7.4	26.8	162	807	17.1	9.13	calcite, dolomite, hematite, kaolinite, smectite, amorphous
Paaloa	rhodic kandiudult	5.0	53.8	205	741	40.0	6.29	anatase, gibbsite, goethite, hematite, illite, kaolinite, maghemite, quartz, amorphous
Leilehua	ustic kanhaplohumult	4.7	17.0	120	863	44.0	5.54	gibbsite, geothite, hematite, illite, kaolinite, quartz, amourphous

[a] Guo, 1997. [b] Soil/water ratio = 1/1 (g/mL). [c] In gram per kilogram. [d] Air-dried [(grams of water per gram of oven-dried soil) × 100].

into a sample cartridge, which is automatically filled with an extraction fluid, and is statically extracted at elevated pressures (500–3000 psi) and temperatures (50–200 °C) for a short period of time (5–10 min) with a minimal amount of solvent (approximately 15 mL per extraction cycle). PFE can also avoid the problems of localized heating and multiple washing steps associated with sonication.

PFE has been previously shown to be equivalent to the automated Soxhlet extraction of base, neutral, and acid compounds and chlorinated pesticides (Ezzell et al., 1995; USEPA, 1996; Richter et al., 1996; Schantz et al., 1997; Berset et al., 1999; Bjorklund et al., 1999; Wang et al., 1999). PFE is applicable to solid and semisolid samples that can be retained in the cell during extraction (Draisci et al., 1998; Tomkins et al., 1998). However, few PFE procedures for the extraction of chloroacetanilide and nitrogen heterocyclic herbicides in environmental samples have been reported. In this study, we have examined water-assisted PFE method for complete recovery of chloroacetanilide and nitrogen heterocyclic herbicides fortified in four clayey soils and the effect of experimental parameters on recovery. Temperature, pressure, flush volume, static cycle, and sample moisture were investigated to assess the experimental conditions on the performance of PFE.

MATERIALS AND METHODS

Soils. Four soils, Paaloa silty clay, Leilehua silty clay, Honouliuli silty clay, and Nohili silty clay, were collected from Oahu and Kauai Islands, Hawaii. The soil samples were air-dried and ground to pass through a 0.84 mm sieve (U.S. 20 mesh), and stored in sealed glass jars at room temperature. Paaloa silty clay was used in the PFE optimization study. Water contents of the soil were determined by drying the ground samples (10 g) overnight at 105–110 °C. The basic properties of the soil are described in Table 1.

Reagents. Alachlor, Bromacil, Hexazinone, Metribuzin, and Tebuthiuron (Figure 1) were purchased from ChemServices, Inc. (West Chester, PA). Anhydrous sodium sulfate from Mallinckrodt, Inc. (Chesterfield, MO) was baked overnight at 400 °C. HPLC-grade water, methyl *tert*-butyl ether (MTBE), and optima-grade acetone were purchased from Fisher Scientific (Pittsburgh, PA). Compressed nitrogen and air for PFE were from Air Liquide (Honolulu, HI). High-purity helium was obtained from Gaspro (Honolulu, HI).

Standard solutions (1 mg each/mL) of the five compounds were prepared in MTBE and kept at 4 °C.

PFE Instrument. A Dionex ASE 200 extractor (Dionex, Salt Lake City, UT) was used in this study. All of the stainless steel extraction cells were in an 11-mL size and were rated at 5 000 or 10 000 psi. The collection vials were either 40- or 60-mL sizes. The sample was loaded into the extraction vessel, which was filled with extraction solvent by opening the pump valve. After the vessel was filled, the pump pressurized the cell. Then, the sample was heated by placing the cell in the preheated oven for 5 min. During heating, thermal expansion
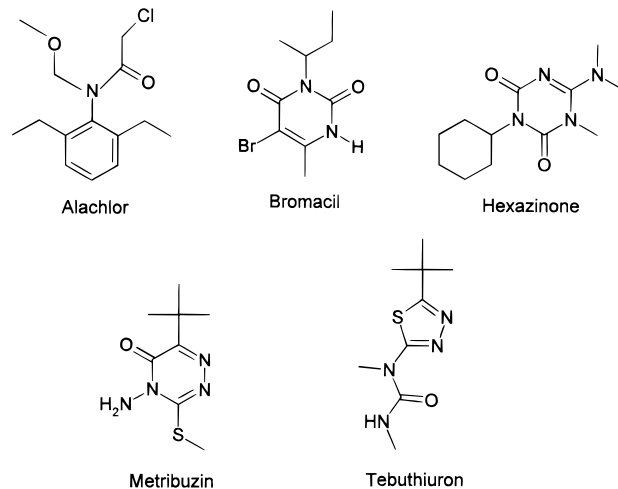
Figure 1. Structures of Alachlor, Bromacil, Hexazinone, Metribuzin, and Tebuthiuron.

of the solvent occurred and increased the pressure. To prevent overpressurization of the cell, the system opened the static valve periodically to regulate the pressure. The solvent that escaped during this venting (0.1–0.2 mL/cycle) was collected in the vial. Since the pump valve remained open, fresh solvent was pumped into the cell to maintain the pressure constant. Static extraction continued for 5 min after the cell temperature was equilibrated to the oven temperature. Then, solvent flush and gas purge steps followed.

PFE Optimization. A Paaloa soil sample (5 g equiv, air-dried) was spiked with 0.5 mL of a 25 μg/mL mixed-standard solution of Bromacil, Hexazinone, and Tebuthiuron. Soil moisture was adjusted to a final content of 6.3 (air-dried)–45%. The soil sample was held at ambient temperature for 1 h and mixed two to three times during this equilibration period. The spiked sample was completely transferred to an 11-mL stainless steel extraction cell, which had a cellulose disk at the outlet end and 2-mL of Ottawa sand on the top of the disk, and any extra volume was filled with Ottawa sand at the inlet end of the cell. The extraction pressure and temperature and the ratio of the water to soil sample were optimized by varying one parameter at a time while the others held at experimentally optimum values.

PFE of Freshly Spiked Samples. A sample (5 g equiv, air-dried) was weighed into a 10-mL beaker and spiked with 0.5 mL of a 25 μg/mL mixed-standard solution of Bromacil, Hexazinone, and Tebuthiuron. Water content was adjusted to 37.6%. The sample was mixed well and covered with aluminum (Al) foil. After the sample was incubated for 1 h, it was transferred to an 11-mL stainless steel extraction cell, which had a cellulose disk at the outlet end and 2 mL of Ottawa sand on the top of the disk, and extracted with pure acetone. Ottawa sand was used as a barrier to fill the extra volume at the inlet end of the extraction cell. The cell containing the sample was prefilled with solvent and then underwent a 5-min oven heating and a 5-min static extraction. The sample was statically re-extracted. The extraction pressure and temperature

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were 1500 psi and 100 °C, respectively. After each heating and static extraction cycle, the static valve was opened, and fresh solvent (approximately 8 mL) was introduced for a period of 10–15 s following by a purge with nitrogen gas at 150 psi for 60 s. The total extraction time was approximately 22 min, and the final volume of the extraction solvent was approximately 32 mL/sample. The extract was collected into a precleaned 60-mL collection vial.

PFE of Aged Samples. Four clayey soil samples (5 g equiv, air-dried) in 10-mL beakers were separately spiked with 0.5 mL of a 25 μg/mL mixed-standard solution of Alachlor, Bromacil, Hexazinone, Metribuzin, and Tebuthiuron in nine replicates. After the moisture was adjusted to 37.6%, the samples were mixed thoroughly, covered with Al foil, sealed with Teflon film, and stored at −20 °C. Three spiked samples of the four soil series were extracted at 2, 7, or 30 days after fortification.

Soxhlet Extraction. A Paaloa soil sample (5 g equiv, air-dried) was spiked with 0.5 mL of a 25 μg/mL mixed-standard solution of Alachlor, Bromacil, Hexazinone, Metribuzin, and Tebuthiuron and Soxhlet-extracted for 18 h with 250 mL of acetone in accordance with EPA method 3540 (USEPA, 1996).

GC-MS Determination. The extracts were dried over anhydrous Na_2SO_4 (10 g) and filtered through GHP Acrodisc filters (0.45 μm × 25 mm) into a 125-mL round-bottom flask. The extracts were concentrated to 1–2 mL using a rotary evaporator. A 25-mL aliquot of MTBE was added in the flask, and the resultant mixture was concentrated to 1–2 mL. This process was repeated once. The concentrated extracts were quantitatively transferred to 5-mL graduated centrifuge tubes and adjusted to 5 mL with MTBE. The extracts were stored at 4 °C until GC-MS analysis.

A Hewlett-Packard (HP) model 6890 series gas chromatograph equipped with a HP model 5973 mass selective detector (MSD), a HP 7673 series injector, a HP 7683 series autosampler, a HP-5 MS fused silica column (30 m × 0.25 mm i.d., 0.25-μm film thickness), and a HP Chemstation data analysis software were used for the analyses. Samples (1 μL) were injected and chromatographed starting at 100 °C for 1 min. The temperature was increased at 7.5 °C/min to 300 °C and held for 2.33 min. The carrier gas was helium at a linear gas velocity of 37 cm/s (constant flow of 1 mL/min). The multiplier voltage on the mass spectrometer was held at 1388 eV (autotune voltage). The MS was operated under electron impact (EI) mode with a 70 eV ionization voltage. Mass spectral libraries were used for identification (Wiley 138K and NIST 99K). Quantification using the external standard calibration was based on selected ion monitoring (SIM) mode as follows: Alachlor m/z 160, 188, 269; Bromacil m/z 205, 231, 260; Hexazinone m/z 171, 172, 252; Metribuzin m/z 198, 214; and Tebuthiuron m/z 156, 157, 171. Dwell time for the different ion groups was 100-ms.

RESULTS AND DISCUSSION

PFE Optimization. The herbicides Alachlor, Bromacil, Hexazinone, Metribuzin, and Tebuthiuron are considered slightly polar chemicals. They are common pollutants found in the environment. In Hawaii, Bromacil and Hexazinone are two of the most widely used herbicides in pineapple culture. Hexazinone and Tebuthiuron are used for control of non-native pest weeds such as *Melastoma candidum, Psidium cattleinum, Rhodomyrtus tomentosa, Rubus arbutus, Lantana camara, Schinus terebinthifolins* (Christmasberry), *Melinis minutiflora* (molasses grass), *and Schizachyrium condensatu.* In this study, Bromacil, Hexazinone, and Tebuthiuron were used as model chemicals to optimize PFE conditions.

The effects and appropriate ratios of water to soil were examined for recoveries of Bromacil, Hexazinone, and Tebuthiuron. Soil moisture varied from 6.3 to 45%. Water greatly affected the above pesticide recoveries
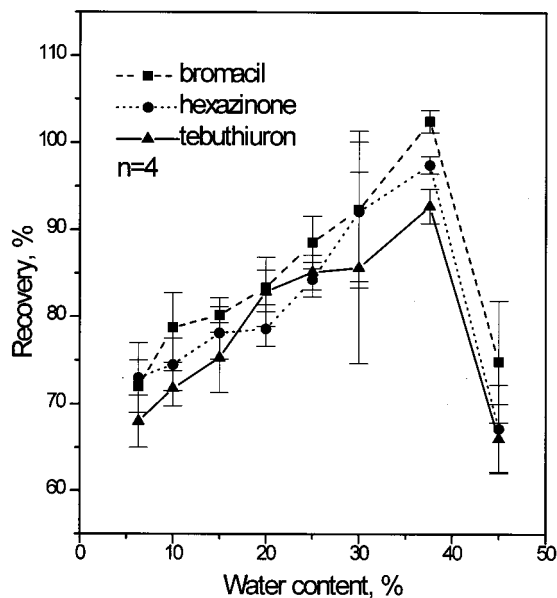

Figure 2. Optimization of soil moisture for PFE of Bromacil, Hexazinone and Tebuthiuron. Paaloa soil (5 g) was treated with an appropriate amount of water (6.3–45%, g/g) prior to extraction. After a 5-min temperature equilibration in the extraction chamber, the fortified samples were extracted for two 5-min static extractions with acetone at 1500 psi and 100 °C following by a 60-s nitrogen purge.

from the soil (Figure 2). Extraction of the air-dried soil (6.3% water) gave recoveries of 72, 73, and 68% for Bromacil, Hexazinone, and Tebuthiuron, respectively. When water content was 37.6%, the method completely recovered the added Bromacil, Hexazinone, and Tebuthiuron. However, average recoveries of the three chemicals dramatically decreased from 93 to 103% to 66–75% when moisture increased to 45%. When soil water content was greater than 40%, the soil extracts were turbid compared to the clear yellow extracts obtained at ≤40% soil moisture, and excess precipitate was trapped from the soil extracts by fitting filter paper at the bottom of the extraction vessel. Some chemicals were possibly adsorbed on the paper filter, and this may result in decreased recoveries. The practical operation may also play a role in low recoveries at higher (>40%) moisture levels. For example, it was very difficult to quantitatively transfer the prespiked muddy soil into the small extraction vessels. Therefore, soil water content greater than 40% was not desirable for the soils in this study.

The extraction efficiency of the three herbicides was further examined to optimize the extraction time and solvent volume when the fortified soil samples were modified with 37.6% water (g/g). The extraction followed two static cycles to collect the extracts in two separate fractions. Bromacil, Hexazinone, and Tebuthiuron in the first fraction accounted for approximately 92, 85, and 83%, respectively, of the spiked amount from the moisturized samples, compared with only 79, 74, and 70% recovery, respectively, when no water was added (Table 2). Water significantly enhanced all the recoveries of the three pesticides, and two static extractions were sufficient for a quantitative recovery. Increasing the PFE flush volume and static time made little difference in the recoveries. This suggested that the incomplete recoveries may not be due to the solvent diffusion limitations or kinetic effects and were consis-

Table 2. Effect of Water on Extraction Efficiency of Bromacil, Hexazinone, and Tebuthiuron as Examined by the Recovery in Fractions of Two Static Extractions

	recovery ± SD,[a] %					
	without water[b]			with water[b]		
analytes[c]	1st static	2nd static	total	1st static	2nd static	total
Bromacil	79 ± 1	2 ± 3	83 ± 6	92 ± 1	7 ± 2	104 ± 7
Hexazinone	74 ± 3	9 ± 2	81 ± 6	85 ± 1	12 ± 1	107 ± 5
Tebuthiuron	70 ± 1	6 ± 5	75 ± 2	82 ± 4	11 ± 1	94 ± 4

[a] SD = standard deviation; n = 4. [b] PFE conditions: 100 °C, 1500 psi, prefill method, 100% of the extraction cell volume of solvent acetone was pumped into the cell, 5-min temperature equilibrium, 5-min static extraction, 60-s nitrogen purge, air-dried soil (5 g) was treated with or without 37.6% water (g/g) prior to the first extraction. [c] Spiked level = 2.5 μg/g.
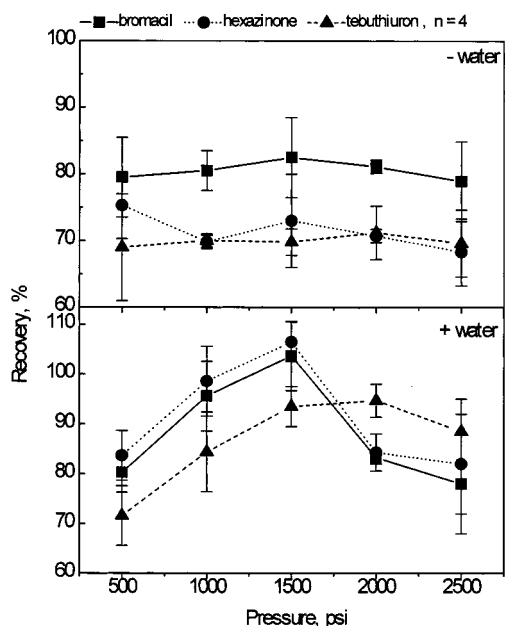
Figure 3. Effect of pressure on extraction efficiency of Bromacil, Hexazinone, and Tebuthiuron. Soil moisture was 37.6%, and the PFE conditions, except for pressure, were the same as those described in Figure 2.

tent with previous findings in SFE studies (Koskinen et al., 1995; Guo et al., 1999).

The effects of pressure on recoveries of Bromacil, Hexazinone, and Tebuthiuron were investigated by extracting soil samples with and without the addition of 37.6% water at pressures ranging from 500 to 2500 psi (Figure 3). A minimum pressure is needed to maintain the solvents as liquids at or above their atmospheric boiling points. The pressures do not need to be excessive. Little effect of pressure on recoveries of the three pesticides was observed when no water was added to the air-dried soil (Figure 3). However, pressure was found to be critical to the moisturized soil extraction. The recoveries increased from 80 to 104%, 84 to 106%, and 72 to 94% for Bromacil, Hexazinone, and Tebuthiuron, respectively, in the water-treated samples as the pressure increased from 500 to 1500 psi. These data confirmed the hypothesis that the increased extraction pressures will effectively enhance the dissolution of the analytes from the soil relative to that at atmospheric pressure. However, extraction of moisturized samples at high pressures (>2000 psi) often caused sample compactness, particularly for fine soils. Tebuthiuron, however, showed smaller variation of recoveries
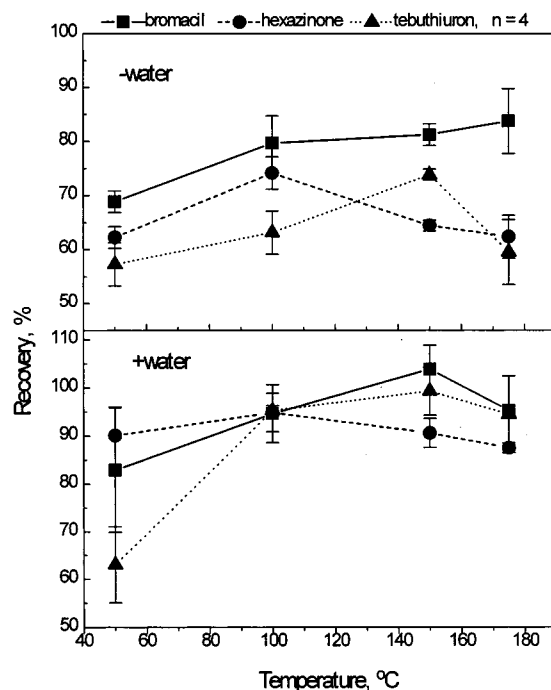
Figure 4. Effect of temperature on extraction efficiency of Bromacil, Hexazinone, and Tebuthiuron. Soil moisture was 37.6%, and the PFE conditions, except for temperature, were the same as those described in Figure 2.

over the pressure range than those of Bromacil and Hexazinone (Figure 3). This may be attributed to the difference in the chemical and physical properties of the three herbicides. Optimum pressures for these three compounds were about 1500 psi, which was used for the remainder of this study.

A set of experiments were performed to investigate the effect of temperature on the recoveries of Bromacil, Hexazinone, and Tebuthiuron at the following conditions: prefill method, acetone as extraction solvent, 1500 psi, 5-min static extraction after equilibration and followed by another static extraction, 5 g of soil samples with or without modification to 37.6% water, an 11-mL stainless steel cell, and 32 mL of solvent used for each extraction. The extraction temperature varied from 50 to 175 °C in the different experiments. Temperature greatly affected Tebuthiuron recovery from soil (Figure 4). The method quantitatively recovered the fortified Tebuthiuron (95−99%) from the moisturized (37.6%) soil when the extraction temperature was 100−175 °C. When temperature was 50 °C, the Tebuthiuron recovery decreased to 63%. Extraction of air-dried soil (6.3% water) gave Tebuthiuron recoveries of 57−74% when the extraction temperature was 50−175 °C (Figure 4). When no water was added, the average recoveries varied in a range of 69−84% for Bromacil and 62−74% for Hexazinone at the extraction temperature of 50−175 °C. Good recoveries of Bromacil and Hexazinone (83−104%) were obtained from the moisturized soil samples at the extraction temperature varying from 50 to 175 °C (Figure 4). There are two possible explanations for the results: The elevated temperatures increase the solvating power of the solvent, the solubility of water in organic solvents, the solvent diffusivity, and the mass transfer rate. Hence, extraction efficiency is increased at elevated temperatures and pressures. Increased temperatures can also disrupt the solute−matrix interactions, decrease the viscosity of solvents and surface

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Table 3. Comparison of Recoveries of Five Chloroacetanilide and Nitrogen Heterocyclic Herbicides[a] from Paaloa Silty Clay Soil Samples by PFE and Soxhlet Extraction

	recovery ± SD,[b] %	
analytes	PFE[c]	Soxhlet[d]
Alachlor	92 ± 6	90 ± 6
Bromacil	104 ± 7	91 ± 6
Hexazinone	107 ± 4	96 ± 3
Metribuzin	86 ± 6	88 ± 5
Tebuthiuron	94 ± 4	92 ± 8

[a] Spike level = 2.5 μg/g. [b] n = 4. [c] PFE conditions: 100 °C, 1500 psi, prefill method, two static cycles, acetone (32 mL) as solvent, total time 22 min, modifier (37.6% water) was added on air-dried soil (5 g). [d] Acetone (250 mL) as solvent, extracted for 18 h.

tension of the solvent and matrix, therefore, allowing analytes to be more quickly dissolved in the solvent. An optimum range of PFE extraction temperatures for these three pesticides was from 100 to 150 °C.

Comparison between PFE and Soxhlet Extraction. Soxhlet extraction is a standard method for trace organics in soils and sediments for environmental analysis. Automatic systems have been recently developed to speed up extraction processes and reduce solvent consumption. PFE is gaining increasing use in environmental analysis (Lopez-Avila, 1999). In this study, the recoveries of the five slightly polar herbicides obtained under optimum PFE conditions are quite comparable to those obtained with Soxhlet extraction (Table 3).

PFE of Compounds Aged in Soils. The PFE procedure was further evaluated for recovering Alachlor, Bromacil, Hexazinone, Metribuzin, and Tebuthiuron aged in four silty clay soils. One of the major processes governing the fate of pesticides in the environment is the retention of pesticides in soils. Thus, extraction is essentially the breaking of bonds between a chemical and soil surface, thereby releasing the chemical into the solvent. Aging often makes pesticides bind with a soil matrix tightly, and thus, it is difficult to quantitatively extract the analytes of interest. For this reason, the PFE conditions for extracting compounds from aged soil samples may be different from those for freshly spiked soils. Few PFE studies were found for the understanding of specific interactions between analytes and soils during aging processes. Our method was applied to extract the five herbicides that were aged in the soil for 2−30 days. The spiked soil samples were kept at −20 °C in the dark to reach a system−adsorptive equilibrium while preventing degradation of the analytes during incubation. The recoveries of the five herbicides aged in the four clayey soils averaged from 90 to 100% (Table 4). No significant difference in the recoveries was found either among the three incubation periods or between freshly spiked and aged samples.

CONCLUSION

A PFE procedure was developed for the extraction of chloroacetanilide and nitrogen heterocyclic herbicides in four silty clay soils. The method showed a quantitative recovery for the herbicides Alachlor, Bromacil, Hexazinone, Metribuzin, and Tebuthiuron. The results presented in this study proved that, by using organic solvents at elevated temperatures and pressures, a quantitative recovery can be achieved for pesticides in soil samples. PFE recoveries and standard deviation values were comparable with those of Soxhlet extrac-

Table 4. Average Recoveries of Five Chloroacetanilide and Nitrogen Heterocyclic Herbicides Aged in Four Hawaiian Clayey Soils

aging,[c] days	average recovery[a] ± SD,[b] %				
	Alachlor	Bromacil	Hexazinone	Metribuzin	Tebuthiuron
0	98 ± 6	99 ± 8	100 ± 5	92 ± 6	96 ± 10
2	95 ± 6	97 ± 4	98 ± 3	90 ± 7	96 ± 7
7	93 ± 5	96 ± 3	96 ± 8	91 ± 5	93 ± 5
30	95 ± 3	98 ± 6	100 ± 8	89 ± 9	94 ± 5

[a] Means from extraction of the four Hawaiian clayey soils: Honouliuli, Nohili, Paaloa, and Leilehua series. Every chemical had three replicates for each type of soil, and the PFE conditions were the same as those described in Table 2. [b] n = 9. [c] Samples were spiked at 2.5 μg/g and mixed well, the moisture was adjusted to 37.6%, and the samples were immediately analyzed or sealed and incubated at −20 °C in the dark for 2-30 days prior to extraction.

tion. When general criteria such as extraction time, solvent consumption, and ease of handling are taken into account, PFE is the preferable technique for environmental analysis. The method illustrated in this study is valuable for the analysis of pesticides in the environment.

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